



Universiteit
Leiden
The Netherlands

Towards optical detection of a single electron

Moradi, A.

Citation

Moradi, A. (2021, February 23). *Towards optical detection of a single electron. Casimir PhD Series*. Retrieved from <https://hdl.handle.net/1887/3149275>

Version: Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/3149275>

Note: To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden



The handle <https://hdl.handle.net/1887/3149275> holds various files of this Leiden University dissertation.

Author: Moradi, A.

Title: Towards optical detection of a single electron

Issue Date: 2021-02-23

4

Single-electron control for optical charge detection

We first studied in Chapter 2 the Stark effect caused by an external electric field applied to a molecular crystal in direct contact with the electrodes. In Chapter 3, we discussed how light-induced charging processes in the vicinity of DBT molecules lead to a stable Stark shift in the zero-phonon line in three different host matrices. Our initial goal is to scale down charge sensing to its ultimate limits and detect one electron optically. An essential need for this purpose is combining single-molecule spectroscopy and electronic manipulation of single charges. In this chapter, we describe charge quantization and control in single-electron devices, and their compatibility with optical measurements of a single charge is discussed.

4.1. Single-electron transfer and control

4.1.1. Coulomb blockade

In many electronic devices, the charges flowing under an applied potential are usually considered as non-interacting particles. In contrast to this non-interacting scattering regime, interactions become very important in the so-called Coulomb blockade regime.^{1,2} These interactions make it possible to control and manipulate individual charges. The Coulomb blockade regime requires certain conditions that can be discussed in terms of energy, conductivity, and capacitance. To understand when the Coulomb effect takes place, it is necessary to consider how the charging energy and the device properties scale with the dimensions of the device. In the following, we discuss these conditions.

4.1.2. Charge quantization and charging energy

Let us simplify the system and consider a tiny metallic island placed somewhere in free space (Figure. 4.1.). This system is assumed to be far enough from any leads that the number of charges inside the island is a constant, integer number.³ Since the island is metallic, the charges are distributed on the surface of the island and generate an electric field around it. Assume we want to add an extra electron to the island, the electron must overcome this electric field, and this will cost energy. To calculate the energy, we consider the island as a capacitor with electrostatic energy:

$$E = \frac{Q^2}{2C} = \frac{e^2}{2C} N^2 = E_C N^2, \quad (4.1)$$

where e , N and C are the electron charge, the number of charges and the self-capacitance of the island, respectively. Adding the first electron to a neutral island costs the energy of $E_C = e^2/2C$ that is known as charging energy.²⁻⁵ The origin of the charging energy is the electrostatic energy stored in the field, and which manifests itself as electron-electron interaction due to charge quantization. The charging energy depends inversely on the island capacitance, itself directly related to the size of the island (see next section for more detail). This means that, in small enough islands, electron charging energy will become dominant and charge quantization will become observable.

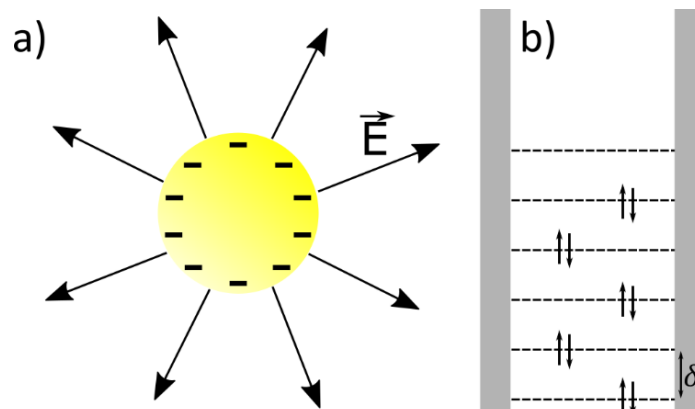


Figure 4.1: a) Charges inside a metallic island create an electric field around it which determines the charging energy. b) Quantum effect of energy level splitting inside a finite island. This quantization of energy is only valid in small island such as molecules.

Charging energy is not the only energy that must be considered when charging the island. Quantum mechanics allows us to express the spacing between energy levels inside the island³ (Figure. 4.1.b). The level spacing at Fermi energy for a box with size of L scales as $\delta \approx \hbar^2/mL^{2.4}$ where m is the electron mass. This relation states that the level spacing inside the island becomes important for very small nanostructures such as molecules and 2D quantum dots.^{1,3} For instance, the energy level splitting in a box with a length of 100 nm is $\delta \approx 10^{-10}$ eV whereas the charging energy for the same box is $E_C = 1.2$ meV. Therefore, for structures larger than molecules, this quantum kinetic energy is often negligible. In the discussions of this thesis, we are not considering the quantum effect and the classical charging energy is the leading of the charge states.

So far, the island was isolated and could store a certain amount of charge. To adjust the number of charges inside the island two bulk electrodes can be added to the system. A source electrode is placed close enough to the island that an electron can jump into it. A gate electrode is placed at a somewhat larger distance from the island to tune the electrostatic potential of the island with respect to the source. This configuration is known as a single-electron box. Figure. 4.2 presents the equivalent circuit of a single-electron box.

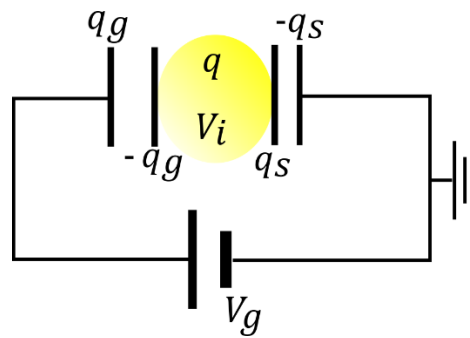


Figure 4.2. Equivalent circuit for an island close to two electrodes acting as source and gate.

The charge stored in the island is

$$q = -q_g + q_s = C_g(V_i - V_g) + C_s V_i = C V_i - C_g V_g, \quad C = C_s + C_g.$$

Therefore, the potential in the island follows from an external potential $V_{ext} = V_g C_g / C$ according to:

$$V_i = \frac{Q}{C} + V_{ext} \quad (4.2)$$

Equation 4.3. shows that the island potential is given by the charge on the island plus the potential induced by the gate. It suggests that the potential of the island, and therefore the number of charges it supports, can be tuned by means of the gate electrode. Note that this potential is not quantized; what is quantized is the charge inside the island.

However, large charging energy is not sufficient to observe clear changes in the charge states of the island. An essential requirement is that electrons do not jump into, or escape from, the

island under thermal fluctuations. This condition is satisfied by ensuring that the charging energy is much larger than the thermal energy:

$$E_C \gg k_B T \quad (4.3)$$

Alternatively, the condition (4.3) is equivalent to demanding that the thermal Johnson noise is much lower than the shot noise due to charge quantization.

4.1.3. Self-capacitance of an island

In the previous section, we showed that the charging energy of an island inversely depends on its capacitance. The self-capacitance itself depends on the geometry and size of the island. In this section, we look at the self-capacitance of two simple shapes of islands that could be used to detect a single electron optically, a sphere and a disk island. The capacitance is defined as $C = Q/V$ and the electric potential V on the surface of a sphere with the radius of R that stores charge Q is $V = -\int_{\infty}^R E \cdot dR$. From electrostatics, we know that the electric field is $E = Q/4\pi\epsilon_0 R^2$. Therefore, the capacitance for a metal sphere is obtained as follow.

$$C = 4\pi\epsilon_0 R \quad (4.4)$$

In a similar way, the potential of a disk island can be calculated analytically, and we have:

$$C = 2\pi\epsilon_0 R. \quad (4.5)$$

Note that these equations are calculated for the conditions under which the islands are in a vacuum. In practice, the dielectric constant of the environment also enters this equation multiplicatively. To have a feeling of the orders of magnitude of the capacitance as a function of these parameters, we give the self-capacitance for different island sizes and the temperature needed to satisfy charge quantization.

Table 4.1: Self-capacitance and maximal thermal energy needed to observe charge quantization, for spherical islands of different sizes.

R	C	E_C	E/k_B
10 μm	6.3×10^{-15} F	12 μeV	0.15 K
1 μm	6.3×10^{-16} F	120 μeV	1.5 K
100 nm	6.3×10^{-17} F	1.2 meV	15 K

4.1.4. Barrier

To manipulate the charges inside the island we need electrodes to add/remove electrons to/from the island. We must now estimate how close the electrodes must be to the island and how strong the resistance of the barrier should be. A first condition gives a lower bound for the resistivity of the barrier and is derived from Heisenberg's uncertainty relation $\Delta E \cdot \Delta t \geq \hbar$. Let us assume that we have paid the charging energy $E_C = e^2/2C$ and added the first charge to the island.

The typical time that the charge stays inside the island should be of the order of the classical discharge time of a capacitor, $RC = C/G$. To have a well-defined state of an extra electron the uncertainty should not exceed the charging energy.^{1,3,4}

$$\frac{e^2}{2C} \cdot \frac{C}{G} \gg \hbar, \quad G \ll \frac{2e^2}{h} = G_Q \approx 10^4 k\Omega \quad (4.6)$$

Where G is the conductivity and G_Q is known as quantum conductance⁶ and appears when the transmission channel width becomes comparable with electron wavelength. Therefore, to prevent electron leakage from the island, it is necessary to have a barrier with conductivity less than the quantum of conductance. Satisfying this condition is relatively easy. For instance, an aluminium oxide barrier thicker than 1 nm would keep charges long enough in the box to measure quantize charge states.

Heisenberg's uncertainty relation defines an upper bound for the conductance of the barrier. A lower bound for the conductance can be defined by the transmission or tunnelling probability. In quantum mechanics the probability of tunnelling through a barrier for an electron is approximately given by a simple $P_t = \exp^{-2\beta l}$, with $\beta = \sqrt{2m(U_e - E_b)/\hbar^2}$, l is the barrier width, m is the electron mass, U_e the electron energy and E_b the potential barrier. This probability decays swiftly as the barrier length increases. As an example, the probability of tunnelling for a barrier of 2 nm is 10^7 times lower than for a 1 nm barrier. A typical tunnelling barrier proper for electrical measurements is between 1 to 3 nm.

4.2. Single-electron transistor

A single-electron transistor (SET) is an electronic device that takes advantage of Coulomb blockade to transfer electrons one by one^{1,3,7}. Its structure is similar to the electron box, except that a third electrode (Drain electrode) is added to conduct the tunnelling current (Figure 4.3).

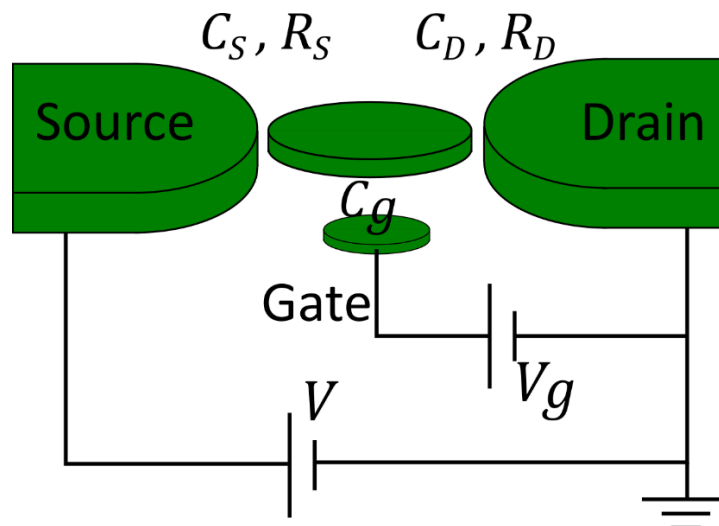


Figure 4.3: Schematic view of a SET. Two electrodes (source and drain) are placed near a cylindrical island. The electron tunnels through the tunnelling junction (typically between 1 to 3 nanometre) and enters the islands. C and R correspond to capacitance and resistivity of the tunnelling junctions. The island energy can be manipulated with a gate electrode, placed far enough to avoid electron transport through it.

The charging energy in a SET is $E_C = e^2/2C_\Sigma$ where $C_\Sigma = C_S + C_D + C_g$. Similar to the electron box, the charge in the island can be calculated in a classical way:

$$Q = CV_i - C_S V_S - C_D V_D - C_g V_g \quad (4.7)$$

with island potential of $V_i = V_{ext} + Q/C_\Sigma$ where the external potential is the potential induced by all the electrodes $V_{ext} = (C_S V_S + C_g V_g + C_D V_D)/C_\Sigma$. Adding extra electrodes introduces extra capacitance that can be even bigger than the self-capacitance of the island. This extra capacitance therefore reduces the charging energy. This inevitable reduction is the price to pay for full control over the tunnelling current and the number of electrons inside the island.³

4.2.1. Current through a SET

The most important feature of SETs for our project, the optical detections of a single charge, is their ability to transmit very low currents and to trap electrons. In this section, we discuss the operation of SETs and we apply this discussion to present our approach for single-charge trapping. Figure 4.4 presents the different working regimes of SETs.

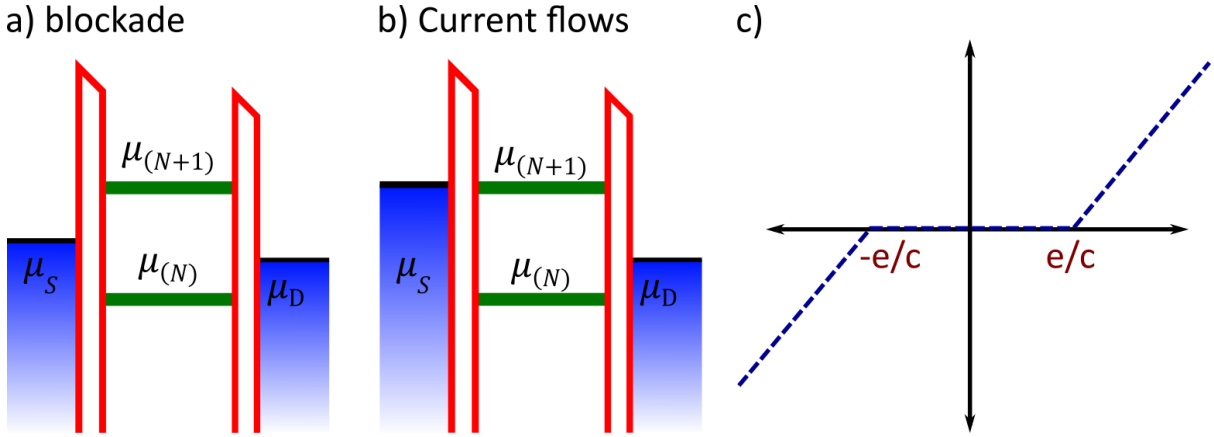


Figure 4.4: Working regimes of SETs. a) Charge transfer is blocked. b) current flows. c) Typical IV curve of a SET.

In order to change the charge state of the island, the electron need to overcome the chemical potential.

$$\mu(N) = (N - \frac{1}{2}) \frac{e^2}{C_\Sigma} - eV_{ext}. \quad (4.8)$$

In the Coulomb blockade regime, the electron does not have enough energy to enter the system. Therefore, the number of charges inside the island stays constant. A source-drain bias voltage will increase the electron energy and at $V = e/C_\Sigma$ electrons reach enough energy to jump into (or out of) the island and current flows. The e/C_Σ value is the maximum threshold and can be suppressed by a gate voltage. Figure 4.4.c shows a typical IV measurement of an SET.

The electron flow becomes more interesting when a voltage is applied to the gate electrode. According to equation 4.8, the number of charges inside the island can be adjusted by the gate voltage. If we draw a 2D map of intensity I as a function of the source-drain voltage V_{SD} and

of the gate voltage V_g the map of Fig. 4.5 follows, which demonstrates the full characteristic of a SET. The white areas in Fig. 4.5 are known as Coulomb diamonds.

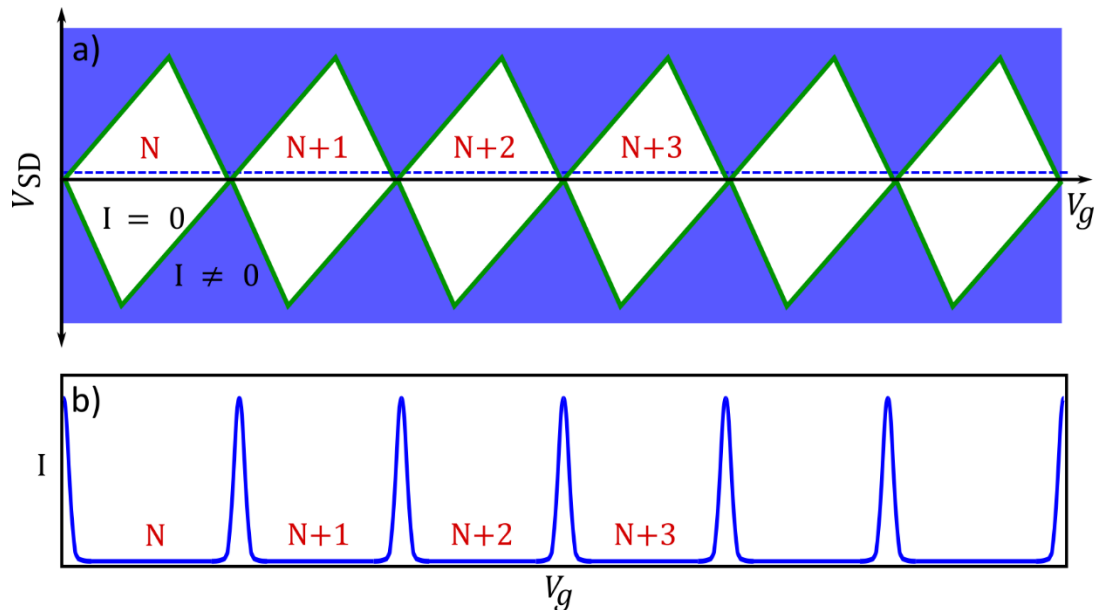


Figure 4.5: a) Schematic view of a typical SET characteristic displaying Coulomb diamonds. Note: the skewness is a result of different C_S and C_D that always exist due to the imperfect structures. b) Schematic of conductance as a function of gate voltage for low bias voltage.

Figure 4.5.a. is a schematic representation of a SET characteristic with typical Coulomb diamonds. Inside a Coulomb diamond (the white area) the current flow is blocked and the number of electrons in the island is fixed. Outside of the Coulomb diamonds the current flows and the number of electrons inside the island fluctuates.

4.2.2. SETs for optical charge detection

In addition to the physical and electrical requirements for building and operating a SET, the optical charge detection we envision adds its own specific requirements. The most restrictive one is that the SET configuration must create a significant electric field at the position of the molecule. This means that the electric field should not be shielded by the electrodes or any other metallic structures close by. This feature rules out many SET configurations and fabrication recipes that have been successfully applied to electrical detection of Coulomb blockade. Accordingly, we had to develop a novel fabrication method to fulfil the electric-field condition.

The ability of electrical controlling of a single charge offers two approaches to detect a single electron optically.

1. By using SETs as an electron trap in the vicinity of an electric-field-sensitive molecule and electrically manipulate the charges inside the island. Figure 4.5.b shows that the current through the island changes from many tunnelling events ($I \neq 0$) to a blockade state that the number of electrons inside the island is fixed by sweeping the gate voltage. Therefore in a low bias for source and drain and by tuning the gate, the SET can be adjusted in a way that maximum current is passing (on top of the peaks in Figure 4.5.b).

In this case, by slightly detuning the gate voltage the electric state changes. For a DBT molecule in DBN placed in the vicinity of the island the electric field of these states is different and the extra electron in the island can be measured optically by measuring the ZPL's Stark shift.

- Alternatively, a low coupled island to electrodes (island far from electrodes) and without a gate electrode that is easier to fabricate can be used to trap electrons. In this configuration the tunnelling barrier and capacitance need to be adjusted in a way that the tunnelling current be significantly low. As we need to distinguish single-electron tunnelling events through fluorescence changes, we will require long intervals between electron tunnelling events, typically a millisecond or longer. A thicker barrier increases the RC time, i.e., the typical time during which an electron remains localized on the island. In addition to the optical single-electron detection, this configuration enables one to measure extremely low current (\leq pA) optically that no electrical ammeter can measure. The following table compares the requirements on SETs and low-coupled island for optical detection of a single charge.

Table 4.2: Characteristic of SETs and SEBs for optical detection of a single charge

	SET	Low-coupled island
Bias Voltage	$> \mu\text{V}$	$> \mu\text{V}$
Tunnelling Current	$> \text{pA}$	$< 0.1 \text{ pA}$
Resistivity	$> 100 \text{ k}\Omega, \cong 1\text{-}3\text{nm}$	$> 10 \text{ G}\Omega, \cong 5\text{-}10\text{nm}$

4.3. Optical detection of an electron by using SET

The DBT/DBN system presented in chapter 2 is an excellent candidate for optical charge detection. In this system, the matrix-induced dipole moment caused a huge Stark shift of about $1.5 \text{ GHz/kVcm}^{-1}$. This sensitivity is sufficient to sense the electric field of one electron over 100 nm. COMSOL simulations were applied to map the electric field distribution around an island in a SET configuration. Figure 4.6 presents the electric field around a 100 nm island that is located 3 nm away from two bulk electrodes. Such a configuration is very similar to the SETs fabricated in our lab for single-electron detection and is discussed in the next chapter.

Considering the DBT:DBN system as the molecular probe for the electric field sensing, a field with a strength of only 80 V/cm could be detected. Based on the COMSOL simulation, the electric field of an island charged by one extra electron is around 100 V/cm at 300 nm away from the island. With the DBT:DBN system, this field could be easily detected as a shift in ZPL more than 3 times bigger than its linewidth. Note that in this estimation the molecule's dipole moment is assumed to be aligned along the electric field vector to obtain the maximum Stark shift. In an unfavourable case when the electric field is projected equally on all 4 possibilities of dipole moment orientation in DBT:DBN system and the Stark shift is minimum ($500 \text{ MHz/kVcm}^{-1}$, see figure 2.5) still a shift in ZPL, more than its linewidth is expected.

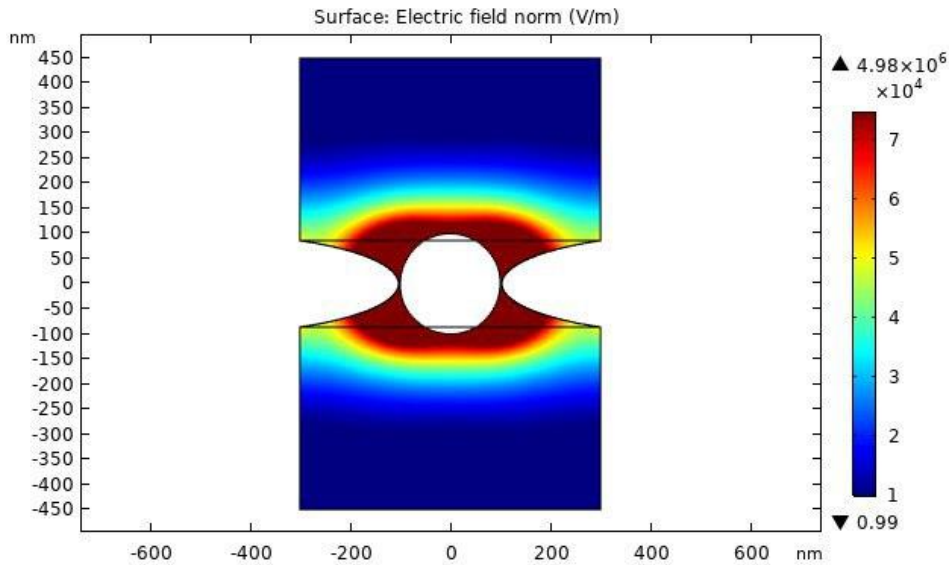


Figure 4.6: Electric field distribution around a 200 nm disc island with two nearby contacts.

4.4. Conclusion

In contrast to the normal non-interacting regime for electric current in a resistance, Coulomb blockade is a result of charge carrier interactions. This interaction defines the charging energy of a finite island hanging somewhere in space. If electrons cannot leave or enter the island spontaneously, the charging energy allows us to manipulate the number of electrons in the islands electrically. We provided the conditions for the Coulomb blockade for a 100 nm disk island at a temperature of 15 K or lower. Adding leads and a gate electrode introduce a controllable electron trap with well-defined states with a controlled number of electrons. The electric field induced by adding one electron to the island is detectable by a sensitive molecule in the vicinity of the island as a shift on its optical transition energy (Stark effect). The electric field induced by the added electron was simulated using COMSOL. We showed that by applying DBT:DBN as the molecular probe for charge detection, shifts larger than the molecular ZPL linewidth are expected at 300 nm away from the island. In the next chapter we discuss the fabrication process of the desired SETs.

References

- (1) Coulomb Blockade. In *Quantum Transport: Introduction to Nanoscience*; Blanter, Y. M., Nazarov, Y. V., Eds.; Cambridge University Press: Cambridge, 2009; pp 211–298. <https://doi.org/10.1017/CBO9780511626906.005>.
- (2) Molen, S. J. van der; Liljeroth, P. Charge Transport through Molecular Switches. *J. Phys.: Condens. Matter* **2010**, *22* (13), 133001. <https://doi.org/10.1088/0953-8984/22/13/133001>.
- (3) Thijssen, J. M.; Zant, H. S. J. V. der. Charge Transport and Single-Electron Effects in Nanoscale Systems. *physica status solidi (b)* **2008**, *245* (8), 1455–1470. <https://doi.org/10.1002/pssb.200743470>.
- (4) Kastner, M. A. The Single-Electron Transistor. *Rev. Mod. Phys.* **1992**, *64* (3), 849–858. <https://doi.org/10.1103/RevModPhys.64.849>.
- (5) Liao, J.; Blok, S.; Molen, S. J. van der; Diefenbach, S.; Holleitner, A. W.; Schönenberger, C.; Vladyka, A.; Calame, M. Ordered Nanoparticle Arrays Interconnected by Molecular Linkers: Electronic and Optoelectronic Properties. *Chem. Soc. Rev.* **2015**, *44* (4), 999–1014. <https://doi.org/10.1039/C4CS00225C>.
- (6) Silva, P. R.; Nassif, C.; Sampaio, M.; Nemes, M. C. Quantum Conductance and Electrical Resistivity. *Physics Letters A* **2006**, *358* (5), 358–362. <https://doi.org/10.1016/j.physleta.2006.05.043>.
- (7) Chen, R. H.; Korotkov, A. N.; Likharev, K. K. Single-electron Transistor Logic. *Appl. Phys. Lett.* **1996**, *68* (14), 1954–1956. <https://doi.org/10.1063/1.115637>.

